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SO_2-catalyzed steam pretreatment enhances the strength and stability of softwood pellets

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HIGHLIGHTS

- ▶ The grinding step can be replaced by a SO_2-catalyzed steam treatment for pelleting.
- ▶ The treated pellets were denser and twice stronger than the untreated ones.
- ▶ The energy input decreased for production of SO_2-catalyzed steam treated pellets.
- ▶ Having higher water affinity, treated pellets did not disintegrate at high humidity.

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ABSTRACT

Densification can partially resolve the logistical challenges encountered when large volumes of biomass are required for bioconversion processes to benefit from economies-of-scale. Despite the higher bulk density of pellets, their lower mechanical strength and sensitivity to moisture are still recurring issues hindering long term transportation and storage. In this study, we have evaluated the potential benefits of SO_2-catalyzed steam treatment to achieve both the needed size reduction prior to pelletization while improving the stability of the produced pellets. This pretreatment substantially reduced the particle size of the woodchips eliminating any further grinding. The treated pellets had a higher density and exhibited a two-time higher mechanical strength compared to untreated pellets. Despite a higher moisture adsorption capacity, treated pellets remained intact even under highly humid conditions. The high heating values, low ash content and good overall carbohydrate recovery of treated pellets indicated their potential suitability for both biochemical and thermochemical applications.

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1. Introduction

Escalating greenhouse gas emissions and concerns over climate change due to an extensive use of fossil fuels have motivated industrialized economies to seek clean energy solutions for their sustainable development. In this context, lignocellulosic-based biofuels are currently being developed as a sustainable alternative to the use of fossil fuels for transport (Solomon and Johnson, 2009). One of the challenges with any future biomass-to-fuels/chemicals process will be achieving access to the substantial amounts of biomass that will be required to benefit from the economics of scale that are inherent in the traditional oil based refinery process.

Raw cellulosic feedstocks are typically bulky (75–200 kg/m^3) and have a high moisture content (~50%) (Mani et al., 2006). These two undesirable characteristics alone make raw biomass costly and difficult to be stored, transported and fed into a reactor. Earlier work (Mani et al., 2006) has shown that one way to improve the economics of transporting biomass over long distances is to pelletize the material. Their higher bulk density (600–800 kg/m^3), lower moisture content (5–8%) and ease of handling should make wood pellets an attractive commodity for the biofuel/bioenergy processes. Due to these benefits, wood pellet production and export have experienced a rapid growth, as demonstrated by the ever increasing global production and trade in wood pellets (Bradley et al., 2011). In 2010, 37 Canadian pellet plants operated at about 65% of their capacity, producing about 1.3 million metric tons (t) per year. Pellet production increased in 2011 when almost 1.9 million t of pellets were produced and exported to Europe, USA

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and Japan for heat and power generation while some of the pellets going to the USA were used for animal bedding (Bradley et al., 2011).

While already a preferred feedstock for combustion to produce heat and power from biomass, wood pellets can also, potentially, be used as a feedstock for bioconversion to produce fuel and chemicals via biochemical pathways. We have recently studied the suitability of commercial wood pellets as feedstocks for liquid biofuel production (Kumar et al., 2012). This earlier work showed that pelletization did not influence the carbohydrate content of softwood feedstocks significantly. In addition, wood pellets could be processed with similar ease as wood chips during a typical bioconversion process, involving a steam pretreatment and subsequent enzymatic hydrolysis, to give comparable fermentable sugar yields (Kumar et al., 2012). Rijal et al. (2012) investigated the influence of pelletization, dilute acid and aqueous ammonia pretreatments of Switchgrass on bioconversion. They found that pelletization significantly increased the sugar yield from ammonia pretreated biomass whereas pelletization had only a marginal improvement on dilute acid pretreated biomass. Theerarattananoon et al. (2012) also studied the effects of pelleting conditions on chemical composition and sugar yield of corn stover, big bluestem, wheat straw, and sorghum stalk pellets. They showed that changes in pelleting parameters and dilute acid pretreatment can influence the sugar yields.

It is recognized that, despite a considerable increase in the bulk density achieved by densification, the pellet durability still need to be further enhanced for their effective handling and storage (Lehtikangas, 2001). Improved mechanical strength and higher stability reduces the generation of fines and minimizes the loss of material during transport, storage and subsequent handling. Broken pellets and dust aggravate problems associated with health and dust explosion in pellet plants (Vinterback, 2004). In addition to potential explosions, fines inhalation is an occupational health problem. Wood pellets tend to adsorb moisture from the surrounding humid air or when exposed to rain. Moistened pellets readily disintegrate and provide an environment for microbial activities and subsequent decay (Rupar and Sanati, 2005). Thus, the affinity of wood pellets to water is a serious concern for an exporting country like Canada where wood pellets travel long distances often over oceans. Therefore, minimizing the disintegration of pellets upon moisture adsorption and improving the mechanical strength are as important as increasing the energy density of the biomass. All these objectives have to be met with minimum energy input during the size reduction, drying and subsequent densification steps.

Pellet durability reflects the binding strength of the material. Non-catalyzed steam treatment of the saw dust prior to pelletisation has previously been shown to improve the mechanical strength and hydrophobicity of wood pellets (Shaw et al., 2009; Adapa et al., 2010; Lam et al., 2011; Biswas et al., 2011). Earlier work has reported that lignin acts as an effective binding agent that contributes to the strength of the densified material (Lehtikangas, 2001; Angle‘s et al., 2001). Kaliyan and Morey (2006) suggested that lignin redistributes during steam pretreatment, forming droplets on the fiber surface. The redistribution of lignin facilitates a stronger binding between biomass particles during subsequent pelletization (Donohoe et al., 2008). It is also likely that the surface lignin distribution improves the hydrophobicity of the steam pretreated material (Angle‘s et al., 2001; Donohoe et al., 2008). Earlier work (Shaw et al., 2009) has shown that pellets made from steam-exploded poplar wood resisted higher breaking forces than did the untreated pellets. In related work, Lam et al. (2011) concluded that pellets made from ground Douglas fir particles, treated with high pressure steam at 220 °C for 5 min were harder and more dimensionally stable than were pellets made from untreated Douglas fir. However, grinding the wood chips followed by a steaming and a subsequent densification operation demanded higher amounts of energy, thus limiting the economic attractiveness of the overall process (Lam et al., 2011). To the knowledge of authors, SO_2-catalyzed steam treatment of wood for pellet production has not been investigated because wood pellets have been used mainly as a feedstock for heat and power applications.

In the work described below, we have applied SO_2-catalyzed steam pretreatment directly on the woodchips with the dual objectives of obtaining sufficient size reduction required for pelletization and enhance the mechanical strength of the resulting pellets. In this way, the energy required for steaming is expected to be offset by replacing the grinding step while a subsequent densification of the steam pretreated material is expected to provide pellets with higher mechanical strength. We have employed SO_2 as a catalyst to enhance the efficacy of the pretreatment by lowering the required residence time and/or temperature of the process (Bruno et al., 2008). The SO_2-catalyzed steam treatment causes more severe destruction of lignocellulosic softwood structure (Bruno et al., 2008; Brownell and Saddler, 1987).

SO_2 catalyzed steam pretreatment has long been used as an effective pretreatment for the bioconversion of softwoods. The pretreatment efficiently solubilizes the hemicellulosic component while providing a water insoluble cellulose rich fraction amenable to enzymatic hydrolysis. Among several acid catalyst studied, SO_2 was shown to result in its uniform distribution into the wood chips and the unabsorbed, residual SO_2 can be easily recycled back, minimizing the amount of catalyst used (Brownell and Saddler, 1987). This earlier work showed that a fraction of the absorbed SO_2 turns to H_2SO_3 upon contact with water/steam and the H_2SO_3 is subsequently oxidized to sulfuric acid at the high temperature and pressure conditions. Using SO_2 also improves the extent of lignin depolymerization and subsequent redistribution which is expected to facilitate binding between the particles during the pelletization process (Zandersons et al., 2004). Therefore, there is a potential to use SO_2 catalyzed steam treatment for producing high quality wood pellets as well as applying these produced pellets as a feedstock for bio-ethanol production.

2. Methods

2.1. Materials

The biomass material tested in this research consisted of white softwood species, Douglas fir (*Pseudotsugamenziesii*). The freshly cut stem wood pieces grown in British Columbia Canada were brought to the lab and debarked manually, split, chipped and screened to an approximate size of 20 × 20 × 5 mm chips. The chips were naturally dried by spreading them on a stack of wire mesh trays in the lab. Moisture content was determined using the convection drying oven method according to the ASABE standard. The moisture content of the woodchip samples averaged 8% with a variation of ±1% (wet mass basis) as received.

2.2. Experimental plan

The tested woodchips were divided into two groups; one passed to the densification process without any pretreatment, and one went through the SO_2-catalyzed steam pretreatment prior to the pelletization. For both cases, different analytical measurements have been done on the ground particles before densification, in order to quantify the compositional changes due to the pretreatment. Also, after pelletization, various properties of produced pellets were measured and compared. The detailed description of each step of the study is explained in the following sections.

2.3. SO_2-catalyzed steam pretreatment

Prior to steam pretreatment, the wood chips were impregnated by adding a specified amount (about 12 g) of SO_2 (4% wt/wt of the substrate) to sealable plastic bags containing 300 g dry weight of chips (Bruno et al., 2008; Ewanick et al., 2007). Once the desired amount of SO_2 entered the bag, the bag was immediately sealed and left for approximately 12 h before steam treatment. After 12 h, the bags were opened in the fume hood and let the residual SO_2 escape for 60 min. The amount of SO_2 retained in the biomass was calculated by weighing the substrates with absorbed SO_2. In the current study, the 56 ± 1% SO_2 uptake by the wood chips was obtained. The studies to minimize the SO_2 loading and reduce the time of impregnation for an effective steam pretreatment are in progress. The work has shown promising results with much lower SO_2 loadings so far, and will be presented as a different publication. Steam pretreatment was conducted in a 2 L StakeTech (Stake Tech-Norvall, Ontario, Canada) steam gun at 200 °C for 5 min. This treatment regime had previously been shown to be effective for Douglas fir woodchips (Lam et al., 2011; Kumar et al., 2010). A higher ratio of biomass to steam (1:1.5 w/w) was used to minimize moisture uptake by the solid in order to minimize post drying of the solids fraction. The higher ratio of biomass to steam was achieved by increasing the amount of biomass aliquots in each batch run to 220 g dry weight of the chips instead of 50 g. This higher solid-steam ratio is a deviation from previous studies (Ewanick et al., 2007; Kumar et al., 2010) where the objective has been to maximize sugar recovery. Instead of having slurry and two fractions of the water soluble (WS) and insoluble (WI), only one wet solid fraction with moisture content of about 60% (w.b.) was recovered after steam treatment. No washing of treated material was done in order to keep the moisture as low as possible. The optimum moisture content (MC) for pelletization was reported between 9% and 15% depending on different feedstock (Relova et al., 2009). The treated material was directly oven dried at 40 °C to reach to the target moisture content of about 10 ± 0.5% for pelletization.

2.4. Analytical analyses

Raw material and SO_2-catalyzed steam treated material were analyzed in triplicate for insoluble (Klason) lignin, hemicellulose and cellulose contents using the modified Tappi T-222 om-88 method as previously described in the NREL-LAP method (Sluiter et al., 2008a). The hydrolysate from this analysis was retained and analyzed for hemicelluloses sugars and cellulose using HPLC (ICS-2500) equipped with an AS50 auto sampler, ED50 electrochemical detector, GP50 gradient pump, and anion exchange column (Dionex, CarboPac PA1). Deionized water at 1 mL/min was used as an eluent, and post column addition of 0.2 M NaOH ensured optimization of baseline stability and detector sensitivity. After each analysis, the column was washed with 1 M NaOH. Twenty microlitres of each sample was injected after filtration through a 0.45 μm syringe filter (Chromatographic specialties, Brockville, Canada). Standards were prepared with seven serial dilutions containing sufficient arabinose, galactose, glucose, xylose, and mannose to encompass the same range of concentrations as the samples. Fucose (0.2 g/L) was added to all samples and standards as an internal standard.

The ash content of each sample was measured in triplicate using NREL method (Sluiter et al., 2008b). For Ash content measurement, about 0.5–1.0 g of completely dried powdered samples were used. The carbon, hydrogen, nitrogen and sulfur contents of both treated and untreated samples were determined on dry basis using a CHNS analyzer (Model 2400 series II, PerkinElmer Company, MA USA). Assuming that only oxygen can be found in the woody material aside from these elements, we calculated the oxygen content by subtracting the sum of these measured components from 100%. The elemental analyses were repeated twice for each untreated and treated material.

2.5. Particle size distribution

The analysis of size distribution for both treated and untreated particles was conducted by sieving in accordance with the ASAE standard S319.4 (ASABE, 2007). Prior to a sieving analysis, samples had been conditioned to 10 ± 0.5% MC. Roughly 20 g of analyzed sample was placed on top of a stack of sieves on a Ro-Tap shaker (Tyler Industrial Products, Cleveland, OH). The sieve series selected were based on the range of particles in the sample (Mani et al., 2006). Sieve mesh numbers used were 20, 30, 40, 50, 70, 100, 140, and 200 corresponding to nominal US sieve openings of 0.841, 0.595, 0.420, 0.297, 0.210, 0.149, 0.105, and 0.074 mm, respectively (ASABE, 2006). The duration of sieving was 10 min, which was previously determined through trials to be optimal (Mani et al., 2006). The mass retained on each sieve and in the pan was weighed on an electronic balance to 0.01 g precision. The sieving test was repeated three times for treated samples and the weighted mean diameter (d_m) of particles was calculated.

2.6. Pelletization

Single pellets were made in a piston-cylinder unit. The assembly consisted of three parts: (1) a piston with 6.32 mm diameter and 90 mm in length, bolted onto a rectangular top surface with four holes on the four corners, (2) an open end cylinder with 6.35 mm inside diameter and 70 mm length, attached to a rectangular bottom surface with four poles on the four corners, (3) a heating tape wrapped around the outer body of the cylinder (Fig. 1a).

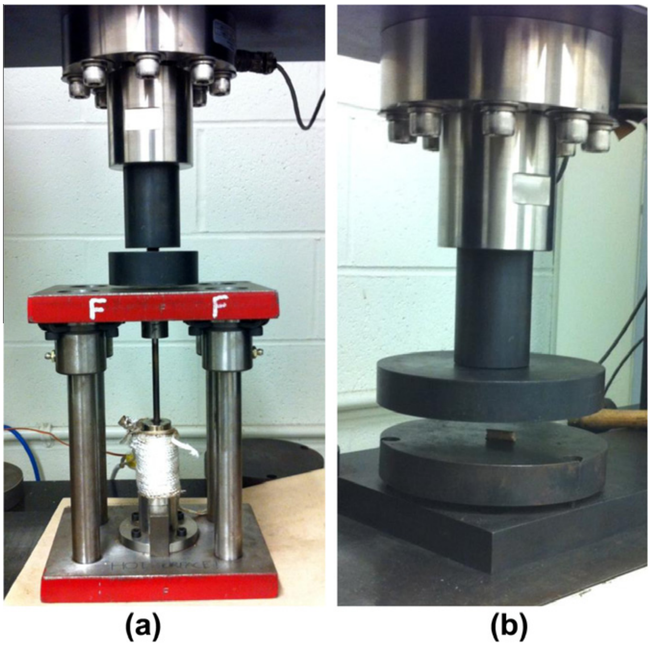

Fig. 1. (a) Pelletization set-up consists of a cylinder piston arrangement. The cylinder is wrapped with electric heating tape. The posts guide the movement and alignment of the piston with respect to the die. The entire assembly is placed under MTI for making single pellet at a time. (b) Hardness test set-up. A single pellet is placed under two platens. The top platen is lowered and forced on the pellet until the pellet disintegrates.

The open bottom of the cylinder was closed during compression by placing a removable block under the cylinder. A 12 mm solid cylindrical spacer placed in the die to rest on the block. The spacer came out of the compression channel by removing the block from the bottom of the die. The body of the cylinder was heated and maintained at about 70 °C. The cavity in the cylindrical die was filled with approximately 0.9 g of biomass using a spatula. The crosshead of a MTI (Measurement Technology Inc., Roswell, GA, model 50K universal) mechanical testing machine pressed on the center of the top surface, so that the four holes were engaged with the four poles and the piston was aligned against the cylindrical die. The MTI was preset to a maximum force of 4000 N on the piston (Tooyserkani et al., in press). The downward measured displacement speed was set at 10 mm/min. From our try and errors, at this speed, the most recordable force vs. displacement curves obtained. The bulk biomass in the cylinder was compressed to the preset maximum force and held for 30 s to arrest the spring back effect of the biomass (Lam et al., 2011). To eject a pellet from the die, the block under the cylinder was removed from the underneath of the pellet and the crosshead's downward motion was reactivated at a speed of 10 mm/min. The piston pushed the formed pellet out of the cylinder. The produced pellet was cooled to room temperature and stored inside a sealed glass bottle for further measurements. In most cases, 20 pellets were made from each steam treated and untreated samples.

2.7. Pellet property measurements

The density of each pellet was measured by dividing its mass over the pellet volume. The volume was calculated by measuring pellet diameter and length using a digital caliper. To evaluate the mechanical strength, each time, one pellet was placed between two steel circular platens under the MTI crosshead (Fig. 1b). The compression was diametrical. The load vs. displacement data to the complete crushing of a pellet was recorded. The maximum force for breakage of pellets was recorded.

Force vs. displacements data during compaction of pellets in the die and during expulsion out of the die was recorded every two seconds. The area under force vs. displacement curves were integrated to yield mechanical energy (*J*) input required to make a pellet (excluding external heat input) (Fig. 2),

$$E = \sum_{i=1}^{n} F_i \cdot \Delta L_i \tag{1}$$

F is force (N) at distance *i* interval, ΔL is deformation at distance *i* interval. The total displacement used in the calculation was from origin to that when the maximum of the force applied to make a pellet was reached. The total displacement used to expel a pellet from the die was 12 mm, the length of the spacer. The energy for compression of a pellet and the energy for expulsion of the pellet were normalized by dividing the calculated energy values by the density of pellets. The results are reported in J/(g/cm^3) or J.cm^3/g. This normalization compensates for variation in volume and mass of each pellet.

The higher heating value (HHV) of solid samples was determined in an oxygen bomb calorimeter (Model 6600, Moline, IL) fitted with continuous temperature recording. A small mass 0.6–1.2 g of densified sample was placed in the instrument chamber. The measurements were repeated three times (on three different pellets).

Moisture adsorption rate of pellets was measured by placing three untreated and three SO$_2$-catalyzed steam treated pellets in a controlled environment chamber (Model LHU-113, ESPEC Corp., Japan). The pellet samples were completely dried initially. The chamber temperature was set at 30 °C with a relative humidity (RH) of 90%. The increase in mass of the sample was monitored and recorded every 10 min for the first hour and every 30 min

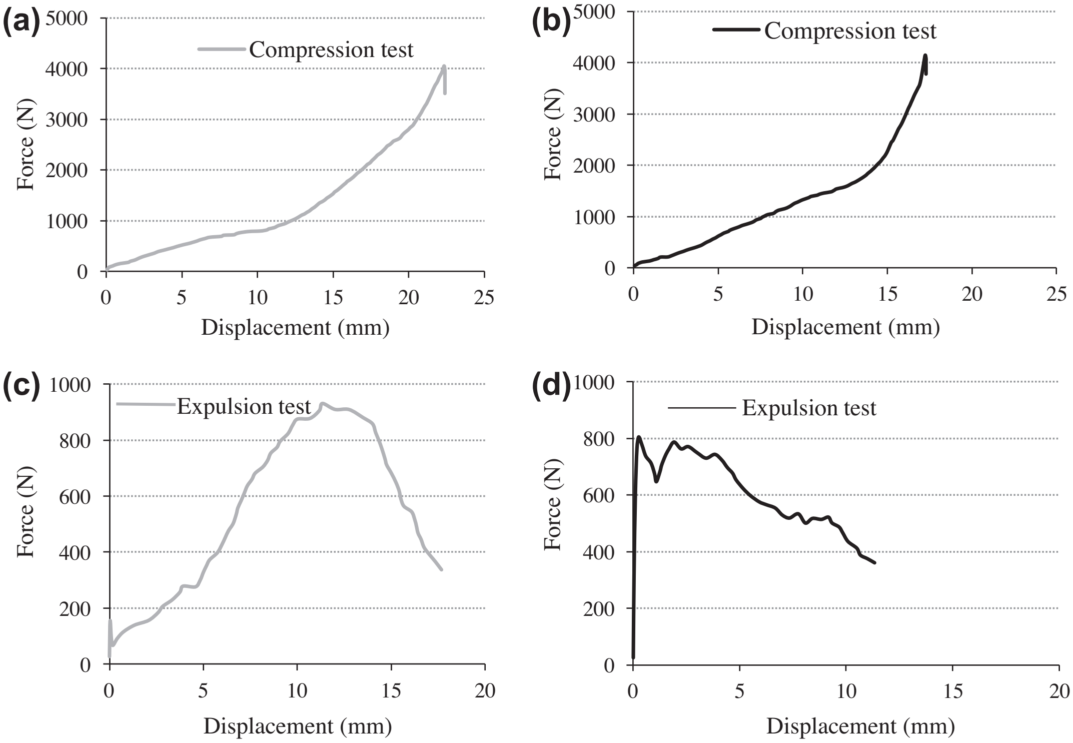

Fig. 2. MTI generated plots of force vs. displacement. The top plots are compression curves for (a) untreated and (b) SO$_2$-catalyzed steam treated particles; the lower plots are the expulsion curves of pellets out of die for (c) untreated and (d) SO$_2$-catalyzed steam treated pellets. The areas under these curves are computed to yield energy input for compression and energy input for pellet expulsion.

afterwards. The weight recording was continued until it reached a constant value (Lam et al., 2011). The moisture content calculated from this final mass was considered as the equilibrium moisture content (M_e) of the material. The kinetics of moisture sorption is represented using the ASABE standard formulation for thin-layer drying (ASAE, 2001),

$$\frac{M - M_e}{M_i - M_e} = e^{-kt} \tag{2}$$

M is instantaneous moisture content (decimal, dry basis), M_e is equilibrium moisture content (decimal, dry basis), and M_i is initial moisture content (decimal, dry basis). Coefficient k is the drying rate constant (min^{-1}), and t is exposure time (min) (ASAE, 2001). For adsorption, $M_i = 0$, Eq. (2) reduces to

$$M = M_e(1 - e^{-kt}) \tag{3}$$

Constant k in Eq. (3) is the adsorption rate constant.

3. Results and discussion

In the work reported here, we compared the quality of pellets made from SO_2-catalyzed steam treated Douglas fir chips with that of pellets made from untreated chips. The energy input to produce pellets was measured and correlated to the physical and compositional characteristics of the pellets. Potential applications of SO_2-catalyzed steam treated pellets were discussed.

3.1. Particle size distribution

As was expected, SO_2-catalyzed steam pretreatment drastically disrupted the rigid structure of woodchips (Fig. 3a and b). The steam pretreated particles were slightly agglomerated after drying, but could be easily separated by hand, while size reduction was visually noticeable (Fig. 3). After untangling the steam treated particles manually, from an approximate size of 20 × 20 × 5 mm for the original woodchips, the particle size was reduced to an overall size of about ~1.1 mm (Fig. 4). Most of the particles were finer in size when compared to the size of the saw dust typically used for pelletization. Boussaid et al. (2000) reported similar degree of particle size reduction after steam treatment of woodchips in the presence of SO_2 catalyst. This degree of particle size reduction was found to be much greater than what was reported previously by Lam et al. (2011) after non-catalyzed steam treatment of Douglas fir chips.

It has been reported that smaller particles with a larger surface area per volume result in an increase particle to particle contact area, thus facilitating a closer packing, resulting in denser and more durable pellets (Mani et al., 2006; Kaliyan and Morey, 2006). As larger particles, greater than 1 mm, generally act as predetermined breaking points in the pellet, an optimum particle size in the range of 0.5–0.7 mm has been recommended (Mani et al., 2006). In contrast, Bergström et al. (2008) have suggested that, under high forces (more than 3000 N), raw material particle size distribution has a minor effect on physical and thermo-chemical characteristics of produced pellets formed from Scots Pine sawdust. These results were of practical importance as if oversized par-

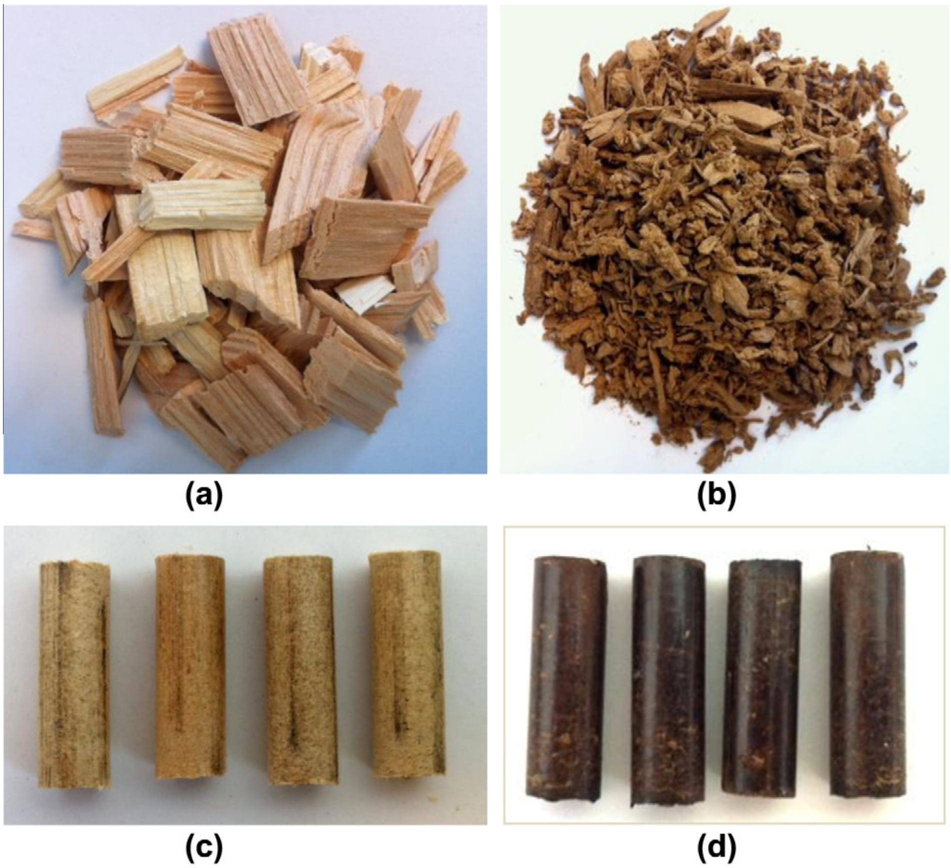

Fig. 3. Appearance of raw material and pellets made in this study: (a) original Douglas fir woodchips, (b) SO_2-catalyzed steam treated and dried woodchips, (c) pellets made from untreated particles and (d) pellets made from SO_2-steam treated particles.

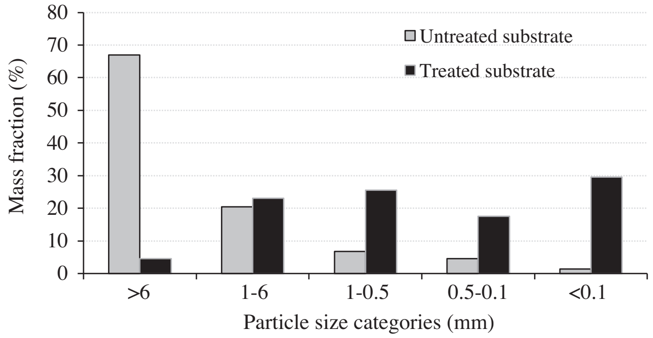

Fig. 4. Particle size distribution for untreated (gray) and SO_2-catalyzed steam treated substrates (dark) before pelletization.

ticles (more than 6 mm) were sieved off, the grinding process could be eliminated resulting in a cost reduction (Bergström et al., 2008). The work reported in this paper suggested that grinding may not be required for SO_2-catalyzed steam pretreated material which might be directly pelletized at 4000 N force load to produce good quality pellets.

3.2. Chemical composition

As was found in our previous work (Kumar et al., 2012), the carbohydrate and lignin content of untreated pellets did not differ considerably from those of woodchips (Table 1). Despite fairly similar chemical composition, a slight decrease in the hemicellulose sugars (Xylan and Mannan) and an increase in the glucose content were observed in pellets compared to woodchips. This was likely due to a loss of hemicellulose sugars from the heat and pressure used during densification as substantial heat is generated from friction between the feed particles and the wall of the die (Kaliyan and Morey, 2006). The compositional analysis of samples after steam pretreatment showed almost complete solubilization of hemicellulose sugars (Table 1) and, as a result, the cellulose and lignin content increased after pretreatment and pelletization (Table 1). Although pelletization slightly reduced the overall carbohydrate content of the biomass, more than 80% of the original carbohydrates were recovered even after steam pretreatment and pelletization. Almost all of the sugars survived the steam pretreatment were also recovered after pelletization (Table 1). As the steam treatment temperature at 200 °C was much higher than that used for pelletization (about 70 °C), the influence of pelletization on the hemicellulose degradation was negligible compared to the effect of SO_2-catalyzed steam treatment (Table 1).

The sum of compounds in Table 1 was slightly lower or higher than 100%. While the >100% mass recovery could be justified as the result of polysaccharide hydration (cleavage of glycosidic bonds) during the treatment, the less than 100% recovery may be attributed to the presence or formation of water-soluble compounds (e.g., extractives and sugar degradation products) that were not quantified here.

3.3. Mechanical properties of the pellets

The mechanical properties of pellets made of steam treated material improved as we expected based on our previous research and published literature (Shaw et al., 2009; Lam et al., 2011). Table 2 shows that the average pellet density increasing from 1.21 g/cm^3 for untreated pellets to 1.34 g/cm^3 for steam treated pellets. Although Lam et al. (2011) did not observed an increase in density in earlier work on steam treated Douglas fir, the addition of the SO_2 catalyst in the current work resulted in a reduction in particle size leading to a stronger binding and higher density. The mechanical hardness of the treated pellets it typically represented by the maximum force required to break the pellets and this was almost doubled after pelletizing the SO_2-catalyzed steam treated material compared to the untreated pellets (from 684.8 to 1341.6 N) (Table 2). This increase was substantially higher than what has been reported previously (Shaw et al., 2009; Lam et al., 2011). It was apparent that finer particles produced by the SO_2-catalyzed steam pretreatment led to stronger binding during densification. In addition, the higher lignin and the soluble sugars content resulting from the SO_2 catalyzed steam pretreatment likely resulted in more efficient binding, thus improving the mechanical strength of the pellets (Lehtikangas, 2001). As mentioned earlier, lignin has been reported to act as a binding agent that contributes to the strength of densified materials (Angle‘s et al., 2001). It has been shown that SO_2 catalyzed steam pretreatment lowers the lignin's molecular weight, consequently decreasing the glass transition temperature compared to the lignin present in untreated wood (Zandersons et al., 2004). Therefore, the higher degree of lignin softening during the conditions of densification and the higher availability of lignin on the fiber surface probably resulted in stronger bonds between the particles. This led to the observed, higher mechanical strength of the pellets.

3.4. Energy input to make pellets

The energy requirement for densification is largely governed by the two main energy inputs of, compressing the particles to form the pellets (compression energy) and, the energy required to push the formed pellets out of the cylindrical die (expulsion energy).

Table 1
Chemical composition of untreated and steam treated Douglas fir chips and pellets (% dry weight) (numbers in the brackets represents standard deviations for $n = 3$).

Samples	Arabinan	Galactan	Glucan	Xylan	Mannan	Lignin
Untreated woodchips	1.2 (0.0)	2.2 (0.0)	47.3 (0.4)	4.9 (0.1)	11.7 (0.1)	29.8 (0.8)
Untreated pellet	1.3 (0.1)	2.8 (0.1)	48.0 (1.5)	3.7 (0.2)	7.3 (0.3)	30.5 (0.3)
Treated woodchips	0.7 (0.0)	2.0 (0.0)	48.1 (0.7)	2.2 (0.1)	9.7 (0.4)	35.0 (0.2)
Treated pellet	0.6 (0.1)	2.1 (0.1)	49.3 (2.2)	2.2 (0.2)	9.5 (0.6)	33.2 (0.3)

Table 2
Mechanical properties of steam treated and untreated pellets (numbers in the brackets represents standard deviations for $n = 10$).

Douglas-fir sample	Pellet density (g/cm^3)	Max. breaking force (N)	Compression energy (J cm^3/g)	Expulsion energy (J cm^3/g)
Untreated pellets	1.21 (0.01)	684.8 (94.4)	22.4 (1.7)	6.6 (3.3)
Treated pellets	1.34 (0.01)	1341.6 (168.8)	17.9 (2.7)	3.9 (2.1)

When the force vs. displacement for making pellets from treated and untreated biomass was compared, the compression curves (Fig. 2a and b) showed that, for up to 15 mm travel of the piston, the forces were low and increased gradually. Beyond 15 mm, the curves increased substantially over a short distance. The maximum force was reached at about 22 mm whereas for the treated material the maximum force was reached at about 18 mm. The increase in force beyond 15 mm was pronounced for the treated material whereas the increase in force was more gradual for the untreated material.

It was apparent from the plots of force vs. deformation for expulsion of pellets that the untreated and treated feedstocks were substantially different (Fig. 2). The length of the spacer used in the die was 12 mm meaning that it took 12 mm for the end of the pellet to reach the bottom of the die where the pellet emerged. As the pellet exited the die, the forces decreased until the entire pellet fell off the bottom of the die. The initial force required to initiate pushing the pellet out of the die increased gradually for the untreated pellet (Fig. 2c) whereas the initial force to dislodge the pellet for the treated sample (Fig. 2d) increased sharply. The maximum force in both cases exceeded 800 N. The force required to continue the movement decreases in case of the SO_2-catalyzed steam treated pellet and reached the lowest recorded value in 12 mm of expulsion. In case of the untreated pellet, the kinetic friction increased up to 12 mm of expulsion and started to decrease when the pellet started to come out of the die. For an untreated pellet, it took about 18 mm to reach the lowest recorded force during expulsion (Fig. 2c).

Surprisingly, the required compression energy decreased from 22.4 J.cm^3/g for the untreated pellets to 17.9 J.cm^3/g for the SO_2-catalyzed steam pretreated pellets. The required expulsion energy was decreased from 6.6 J.cm^3/g for the untreated pellets to 3.9 J.cm^3/g for SO_2-catalyzed steam pretreated pellets (Table 2). It appears that the fine and brittle SO_2-catalyzed steam treated particles were easily crushed and subsequently compressed during densification to form the pellets. It was likely that the higher degree of lignin redistribution on the surface and the presence of soluble sugars facilitated better binding, requiring less amount of compression energy (Zandersons et al., 2004). In addition to the surface lignin and soluble sugars, a minor fraction of the lignin was probably sulfonated during SO_2-catalyzed steam pretreatment, forming lignosulfonates which potentially acted as a lubricant during the process. A wide range of lubricant additives are known to contain sulfur (Gao et al., 2004) and it is possible that the presence of these 'lubricant like' components eased the expulsion of treated pellets and decreased the energy consumption.

3.5. Moisture sorption properties of pellets

As mentioned earlier, one of the main challenges with commercial wood pellets is their sensitivity to humidity. In the presence of even relatively low amounts of moisture wood pellets tend to fragment, resulting in the loss of structural integrity and shape and possible disintegration during transport and storage. Therefore, we next assessed the stability of the untreated and SO_2-catalyzed steam treated pellets under humid conditions (Fig. 5). It was apparent that the moisture content of the pellets increased exponentially reaching an asymptote, at equilibrium conditions (Fig. 5a). Interestingly, the steam treated pellets exhibited a higher affinity for moisture reaching an ~20% moisture content by weight, which was two times higher compared to that of untreated pellets. However, despite the increase in moisture absorption capacity, the steam pretreated pellets were stable and could hold their integrity after 1 day in a humidity chamber (with a relative humidity of 90%) whereas the untreated pellets lost their integrity after 4 h (Fig. 6a and b). When the pellets were immersed in water, the untreated pellets disintegrated immediately after immersion while the treated pellets remained intact even after a week (Fig. 6c and d). It was apparent that, while the hydrophilic components such as soluble sugars increased the water adsorption capacity of the steam treated pellets the hydrophobic components, particularly the redistributed lignin, provided a coating which lowered the rate of adsorption and maintained the strong binding and integrity of the pellet. The SEM images of untreated and treated Douglas fir particles with 5k magnification also confirmed the changes on the particles surface (the re-condensed lignin droplets on fiber surface) due to the treatment (Angle's et al., 2001).

In previous work, Lam et al. (2011) showed that the equilibrium moisture content (M_e) of untreated pellets dropped from about 10.2% (d.b.) to a minimum of 5.9% (d.b.) for non-catalyzed steam treated pellets. In contrast we found considerably higher (M_e) values for treated pellets (20.6% d.b.) when compared to untreated pellets (9.2% d.b) while the steam pretreated pellets took a longer time to reach equilibrium. In both studies the sorption constant rates decreased. However, the adsorption rate (k) reduction was much higher in the current work, from 0.01 min^{-1} for untreated pellets to 0.001 min^{-1} for SO_2-catalyzed steam treated pellets (Fig. 5b). It appears that the soluble sugars present in the steam

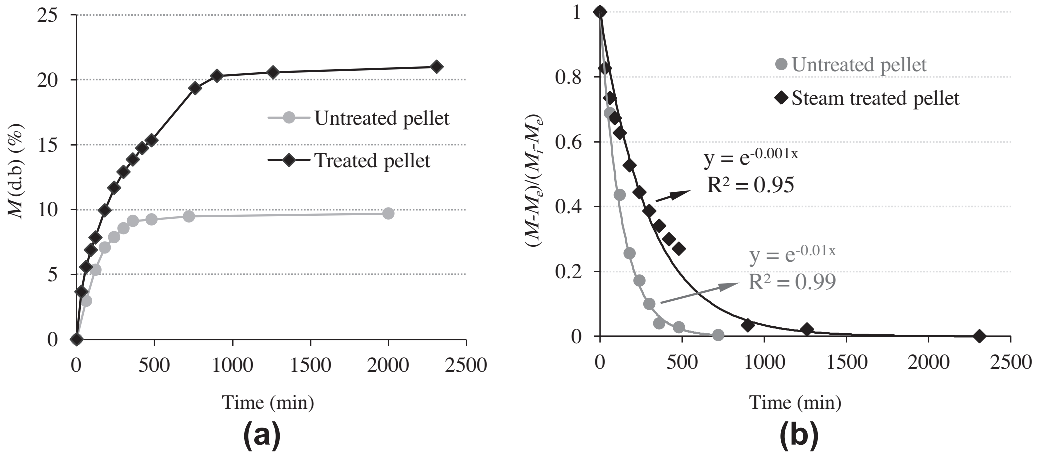

Fig. 5. (a) Pellet moisture content vs. time when placed in the humid chamber (30 °C – 90%). Treated pellets reached to higher equilibrium moisture content than the untreated sample. (b) Moisture adsorption rate constant. Treated pellets reached equilibrium moisture content in longer time.

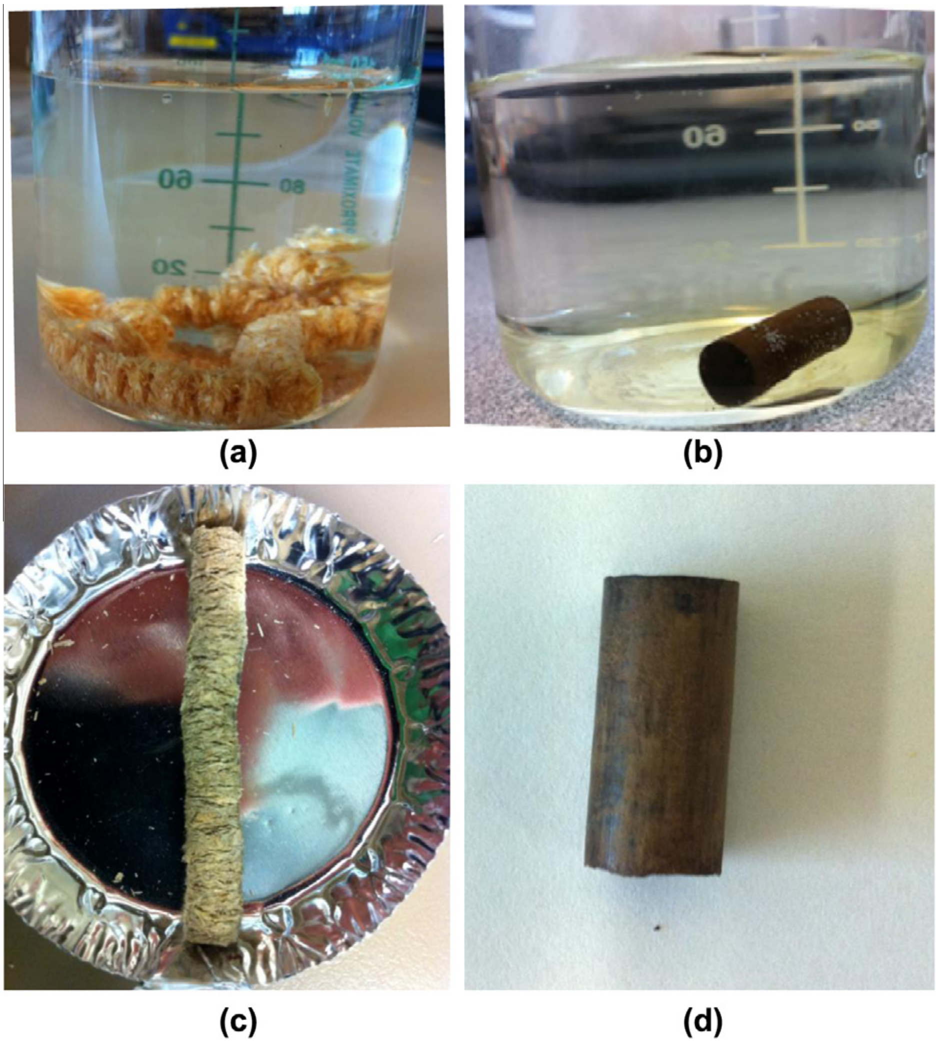

Fig. 6. Moisture sorption tests: (a) untreated pellet right after immersing in water, (b) treated pellet after one week immersing in water, (c) appearance of an untreated pellet reached to equilibrium moisture content in humid chamber (30 °C – 90% RH) after 4 h and (d) unchanged appearance of a treated pellet reached to equilibrium moisture content after 24 h.

pretreated pellets are highly hydrophilic, which would readily adsorb water under humid conditions. This likely resulted in a higher moisture adsorption by the steam pretreated pellets. In addition, it is possible that the SO_2-catalyzed steam pretreatment "opened up" the lignocellulosic matrix more severely and exposed more of the cellulose micro-fibrils such that water could more easily penetrate and be retained by the cellulose. The rougher surface of the particles after the treatment could be observed by the SEM images (Angle's et al., 2001). Several researchers have also shown that sulfur can involve in a hydrogen bond formation similar to oxygen (Francuski et al., 2011). The formation of these additional sites for water adsorption might explain the higher equilibrium moisture content of the treated samples.

3.6. Discussion on practical application of this research

Higher mechanical strength and stability of SO_2-catalyzed steam treated pellets in a humid environment make these pellets desirable for shipping and handling to any biomass-based facility. In our previous study, Kumar et al. (2012) showed that SO_2-catalyzed steam treated pellets were comparable with SO_2-catalyzed steam treated softwood chips in terms of sugar recovery (Table 1) and enzymatic hydrolysis yield at the same conditions. This conclusion has practical importance as the current study showed the much higher stability of these pellets as well. More than 60% of the pellets prepared from steam pretreated softwood were carbohydrates, which indicated that the material could be potentially used for bioconversion applications. Previously, we have shown that an additional steam pretreatment was not required for obtaining the soluble sugar recovery and a reasonable enzymatic hydrolysis of the cellulose fraction (Kumar et al., 2012). In the application of pellets for the biochemical conversion purposes, the necessity of pretreatment step for bioconversion of softwood particles is not negotiable. By applying this pretreatment prior to pelletization, we do not add any new energy to the whole bioconversion process while benefitting from the better logistic of pellets. However, due to the higher mechanical strength of the steam pretreated pellets, a mild mixing should be employed to loosen the treated pellets in water within a reasonable time leading to an efficient fractionation and recovery of the soluble sugars before the enzymatic hydrolysis step. This is while the energy saving on the grinding, shipping and handling steps of highly stable treated pellets is more than enough to compensate the energy required for the mild mixing step in the bioconversion process.

In order to determine the suitability of the pellets prepared from steam pretreated softwood for combustion and co-firing

Table 3
Elemental analysis of samples (numbers in the brackets are standard deviations for *n* = 3).

Douglas-fir sample	Higher heating value (MJ/kg)	Ash (%)	C (%)	H (%)	N (%)	S (%)	O (%)
Untreated pellet	18.6 (0.1)	0.1 (0.0)	46.3 (0.0)	6.5 (0.1)	0.1 (0.0)	0.5 (0.0)	46.6 (0.1)
Treated pellet	18.6 (0.0)	0.6 (0.1)	51.7 (0.2)	5.8 (0.1)	0.1 (0.01)	1.1 (0.1)	41.3 (0.2)

applications, the higher heating values and elemental composition were compared to those of the original pellets (Table 3). It was apparent that the higher heating value of the SO_2-catalyzed steam treated pellets (treated at 200 °C for 5 min) and original pellets were similar ~at 19 MJ/kg and they were generally lower than what has been observed with torrefied pellets (Tumuluru et al., 2011). The good recovery of carbohydrate even after a steam pretreatment and pelletization implied that hydrolysis reactions were more predominant during the pretreatment step (Ramos, 2003). This reaction is less likely to change the heating value of the material whereas, during torrefaction, pyrolysis reactions predominate (Tumuluru et al., 2011). The lower O/C and H/C ratios from the elemental analysis (Table 3) also resembled mild torrefaction conditions. One possible explanation for unchanged heating values, but higher carbon ratios could be the presence of higher sulfur in the treated product (Table 3). The combustion energy of sulfur is much lower than carbon and as a result, can decrease the overall calorific heating value. Despite a slightly higher ash content observed in the steam pretreated pellets, the values were low enough to not raise any issues for any combustion applications. Even though the SO_2 pretreatment has a positive effect on the density and conversion, this pretreatment may have a negative environmental impact when the material is co-fired with coal or used for chemical conversion applications by releasing more SO_2 into environment. However, our optimization study on reducing the SO_2 loading during the pretreatment is in progress and there is a good potential for this reduction. The results of the study to investigate the influence of reduced SO_2 input on subsequent pelletization will be presented in a companion paper.

4. Conclusions

Sulfur dioxide catalyzed steam treatment of woodchips resulted in a substantial reduction in particle size, enabled direct pelletization without any further size reduction step. Subsequent pelletization of this treated material resulted in denser pellets with considerably higher mechanical strength, while minimizing the energy required for densification. The treated pellets remained intact even under high humid conditions, made them more suitable for long term storage and shipping. While high calorific values and low ash content make the treated pellets desirable feedstocks for thermochemical conversion, the good recovery of original carbohydrates from treated pellets make them viable feedstocks for any biochemical-based conversion.

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